Analysis of Sulfur and Phosphorus Compounds with a Flame Photometric Detector on the Agilent 6890 Series Gas Chromatograph

Application

Gas Chromatography

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Abstract

A gas chromatograph (GC) with a flame photometric detector (FPD) is frequently employed in analyzing complex samples for specific compounds. The wavelength filter of the FPD can be set to select for many elements, but it is most commonly used to detect sulfur and phosphorus. This application note discusses the uses of the FPD in gas chromatography, demonstrates the linearity and method detection limits (MDL) of the 6890 Series GC with an FPD, and gives examples of analyses of organophosphorus pesticides using the 6890 GC with an FPD.

Key Words

Gas chromatography, flame photometric detector, FPD, sulfur analysis, phosphate analysis, pesticides, organophosphorus pesticides, EPA method 1618, EPA method 622.

Introduction

The flame photometric detector is one of the most widely used selective detectors in gas chromatography. The FPD consists of a reducing flame that produces chemiluminescent species. These species emit characteristic light that is optically filtered for the desired wavelength; the wavelength selection determines which compound is detected. The filtered light is measured by a photomultiplier and transduced into a signal. A second photomultiplier can be added, which allows simultaneous detection of a second signal.

FPD filters can be selected for many different compounds, but the most common uses are for the selective detection of sulfur and phosphorus compounds in complex mixtures. The selectivity of classical FPDs is typically (as a ratio by weight to carbon) 10^5 for sulfur and 10^6 for phosphorus. The FPD operates over a dynamic range of 1×10^3 for sulfur and 1×10^4 for phosphorus.[1]

Gas chromatography with an FPD can be used to detect sulfur compounds in crude oil and sulfur contaminants in natural gas.

In food analysis it is used to detect off-flavors resulting from the liberation of volatile sulfur compounds. It is also used to simultaneously detect sulfur and phosphorus in chemical warfare agents. In the environmental area, the FPD is used for detection of organophosphorus pesticides and herbicides. Several EPA methods for pesticide detection, including EPA methods 1618[2] and 622[3], specify the use of an FPD.

A schematic of a single FPD for the 6890 Series GC is shown in figure 1. A dual wavelength version is available that has a second photomultiplier mounted perpendicular to the first for simultaneous detection of a second wavelength. The 6890 GC is available with either a single or dual FPD.

The sensitivity of any FPD is affected by detector temperature, flame chemistry, and filter wavelength.

- **Detector temperature**. To protect the photomultiplier, the maximum temperature limit for the 6890 FPD is 250 °C. Photomultiplier tube (PMT) noise increases with setpoint temperature, so the detector temperature should be as low as possible. Generally, the temperature should be set about 25 °C above the highest temperature reached in the oven program. To prevent water condensation and clouding of the window, the minimum operating temperature is 120 °C.[4]

- **Flame chemistry**. FPD sensitivity is highly dependent on detector gas flows. On the 6890 GC, the gas flows are electronically controlled. This allows rapid and precise optimization of flow rates. Sulfur and phosphorus modes have different optimum flow requirements, so the ability to easily set and reset flows increases the quality of results and saves time.
- **Filter wavelength**. For the FPD, filters of specific wavelength are physically installed in the detector. A 394-nm filter is used for sulfur detection, and 526-nm filter for phosphorus detection.

Experimental

All experiments were performed on a 6890 Series GC with electronic pneumatics control (EPC) and an Agilent 7673 automatic liquid sampler (ALS). An Agilent 1707A ChemStation was used for instrument control and data acquisition. Chromatography conditions are shown with the individual chromatograms in figures 2, 3, and 4.

Results and Discussion

Linearity and MDL

In sulfur mode, the response of the FPD is proportional to analyte concentration squared. The calculated MDL and r^2 values from linearity experiments for a single photomultiplier in sulfur mode are listed in table 1, and the chromatogram for a 20–40 ppb sample from the experiment is shown in figure 2. The square of the concentration was used to calculate regression statistics. When using a ChemStation for data analysis, a quadratic calibration fit is used for sulfur.

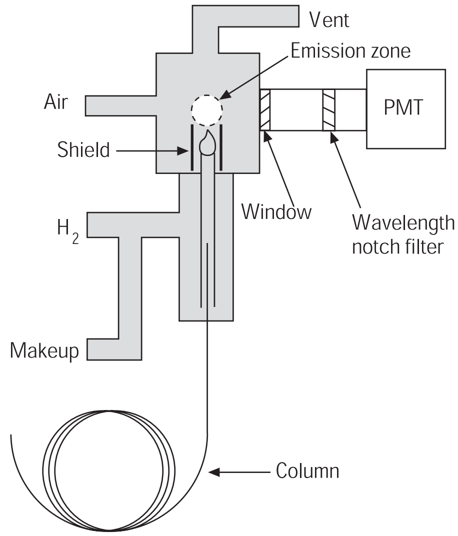

Figure 1. Single photomultiplier tube FPD for 6890 Series GC

Table 1. MDL and Linearity over 10^2 Range Sulfur Mix on the FPD

Peak Number	Compound Name	MDL pgS/sec n = 11	Linearity r^2 n = 15
1	2,5-dimethylthiophene	26.22	0.9986
2	sec-butylsulfide	20.10	0.9983
3	1,4-butanedithiol	22.27	0.9972
4	dodecanethiol	16.90	0.9985
5	octyl sulfide	16.14	0.9979

Conditions

Injection:	1 µL splitless
Oven program:	60 °C, hold 1 minute; 20 °C/min to 250 °C, hold 7 minutes
Single FPD in sulfur mode:	50 mL/min H_2, 60 mL/min air, 60 mL/min N_2 makeup at 250 °C
Column:	HP-5, 30 m x 320 µm at 25 psi constant pressure

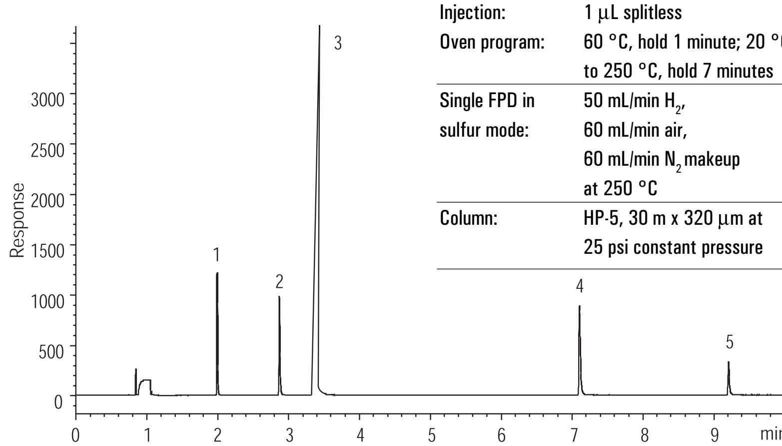

Figure 2. 1 µL of 1.5 ppm sulfur standard, FPD in sulfur mode (The peaks are identified in table 1.)

The response of the FPD is linear in phosphorus mode. Table 2 shows the r^2 values for an organo-phosphorus pesticide mixture and the MDL calculated from the study. Figure 3 shows the chromatogram. A standard linear curve fit is used for phosphorus when using a ChemStation for data analysis.

Analysis of EPA Method 1618

Figure 4 shows the chromatogram obtained from the analysis of organophosphorus pesticides according to EPA method 1618. The injected concentration of each compound was 1–2 ppm.

Table 2. MDL and Linearity over 10^3 Range for Organophosphorus Pesticides on the FPD

Peak Number	Compound Name	MDL pgPesticide/sec n = 11	Linearity r^2 n = 15
1	phorate	1.85	0.9996
2	demeton	1.13	> 0.9998
3	disulfoton	1.31	> 0.9999
4	diazinon	1.74	> 0.9999
5	malathion	1.74	> 0.9999
6	fenthion	1.75	> 0.9999
7	parathion	1.84	> 0.9999
8	trichloronate	2.27	> 0.9999
9	tokuthion	2.51	> 0.9999
10	fensulfothion	–	> 0.9999
11	ethion	1.29	> 0.9999
12	sulprofos	2.36	> 0.9999
13	guthion	1.24	> 0.9999
14	coumaphos	2.08	> 0.9999

Conditions	
Injection:	1 µL splitless
Oven program:	60 °C, hold 1 minute; 20 °C/min to 250 °C, hold 7 minutes
Single FPD in phosphorus mode:	150 mL/min H_2, 110 mL/min air, 60 mL/min N_2 makeup at 250 °C
Column:	HP-5, 30 m x 320 µm at 25 psi constant pressure

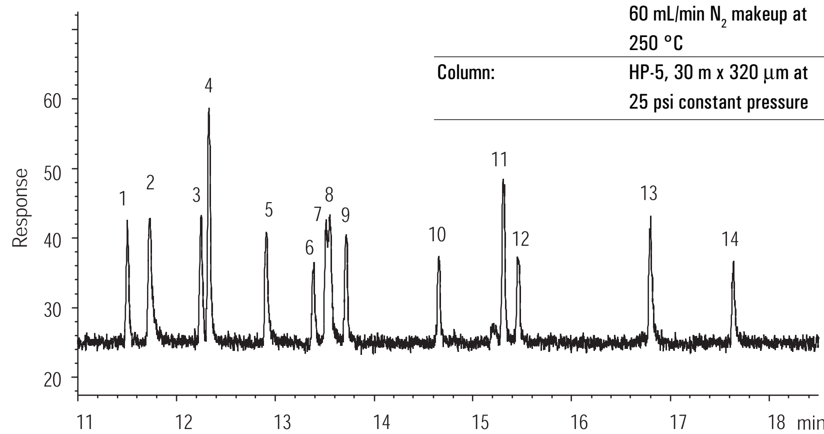

Figure 3. 1 µL Splitless injection of 20–40 ppb organophosphorus pesticide standard, FPD in phosphorus mode (The peaks are identified in table 2.)

Conditions	
Injection:	1 µL cool on-column
Oven program:	60 °C, hold 0.5 minute; 25 °C/min to 110 °C, 3 °C/min to 250 °C, hold 10 minutes
Single FPD in phosphorus mode:	75 mL/min H_2, 100 mL/min air, 60 mL/min N_2 makeup at 250 °C
Column:	1.5 µm HP-1, 30 m x 530 µm, 7 mL/min He constant flow

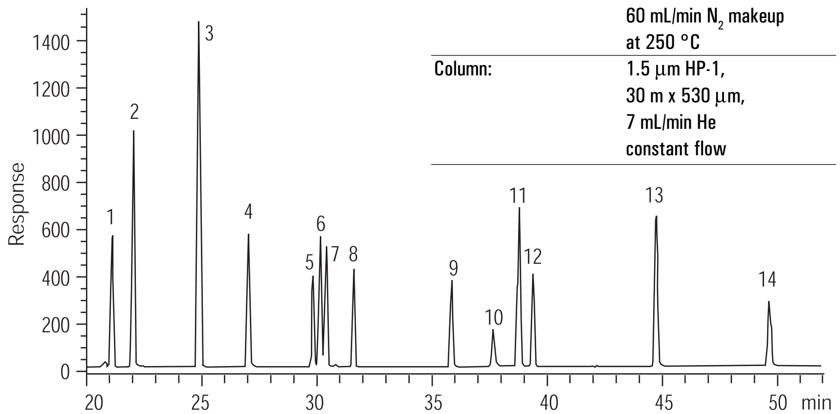

Figure 4. Analysis of organophosphorus pesticides according to EPA method 1618, 1 µL on-column injection of 1–2 ppm standard, FPD in phosphorus mode (The peaks are identified in table 2.)

Conclusions

The Agilent 6890 Series GC with an FPD can be used for the sensitive, and selective measurement of sulfur- and phosphorus-containing compounds in complex mixtures. The electronic pneumatics control on the Agilent 6890 GC ensures rapid and accurate gas flow control, provides for easier method setup and documentation, and simplifies optimization.

References

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